UNIVERSITY OF PENNSYLVANIA

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IN CHEMISTRY

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PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
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Some Tolyl Derivatives of Germanium

Numerous phenyl but relatively few tolyl derivatives of germanium are known.[1]

No ortho or meta tolyl germanium compounds have been reported. A number of para tolyl compounds, mostly of mixed types, have been described by Tabern, Orndorff and Dennis,[2] Schwarz and Lewinsohn,[1] Bauer and Burschkies,[1] and Shelton.[3] Most tetraarylgermanes have been prepared from germanium tetrahalide by arylation either with Grignard compounds or with aryl halides and sodium,[1] both methods giving low yields.[4]

In the present study the interaction of germanium tetrachloride and arylmagnesium bromide led to incomplete arylation, with formation of triarylgermanium halide; a similar result was reported by Morgan and Drew[4] in the preparation of tetraphenylgermane. This procedure was tried unsuccessfully also for the preparation of triphenyl-*m*-tolylgermanium from triphenylgermanium bromide and *m*-tolylmagnesium bromide. The interaction of germanium tetrachloride and *p*-tolylmagnesium bromide further afforded an interesting example of exchange of halogen, the major product being tri-*p*-tolylgermanium bromide. An analogous result was obtained by Bauer and Burschkies[1] for the reaction between cyclohexylmagnesium bromide and germanium tetrachloride.

A much more satisfactory procedure is that first used for tetraphenyltin by Chambers and Scherer[5] and extended by Kraus and Foster[6] to the preparation of tetraphenylgermanium, the first-formed Grignard compound being treated with zinc chloride, and the resulting zinc aryl (without isolation) treated with germanium tetrahalide. By this method there were obtained tetra-*p*-tolyl-, tetra-*m*-tolyl-, and tetra-*o*-tolylgermane in yields of 65, 75 and 30%, respectively. In each case some of the corresponding di-tolyl was isolated. No tri-*p*-tolylgermanium chloride was found, but both tri-*m*-tolyl- and tri-*o*-tolylgermanium chlorides were isolated as by-products due to incomplete arylation. The zinc aryl procedure was used also for the preparation of triphenyl-*m*-tolylgermanium.

The dearylation of tetraarylgermanes by bromine was effected for tetra-*p*-tolylgermanium by Schwarz and Lewinsohn[7] and for the tetra-*o*- and

(1) "Gmelins Handbuch der anorganischen Chemie," System-Number 45, "Germanium," 8th ed., Verlag Chemie, Berlin, 1931, pp. 53–57; R. Schwarz and Lewinsohn, *Ber.*, **64**, 2352 (1931); Kraus and Nutting, *J. Am. Chem. Soc.*, **54**, 1622 (1932); Flood, *ibid.*, **54**, 1663 (1932); Bauer and Burschkies, *Ber.*, **65**, 956 (1932).

(2) Tabern, Orndorff and Dennis, *J. Am. Chem. Soc.*, **47**, 2039 (1925); **49**, 2512 (1927).

(3) Shelton, paper presented at the Washington meeting of the American Chemical Society.

(4) Morgan and Drew, *J. Chem. Soc.*, **127**, 1760 (1925). No other investigators report yields on tetraaryl compounds.

(5) Chambers and Scherer, *J. Am. Chem. Soc.*, **48**, 1054 (1926).

(6) Kraus and Foster, *ibid.*, **49**, 459 (1927).

(7) Schwarz and Lewinsohn, *Ber.*, **64**, 2354, 2358 (1931).

tetra-*m*-tolyl compounds in the present study. In each case the main product was triarylgermanium bromide, some nuclear bromination occurring with the *o*-tolyl compound. Hydrolysis of tri-*m*-tolyl- and tri-*p*-tolylgermanium bromide by aqueous alkali or by alcoholic silver nitrate yielded the corresponding tritolylgermanium oxide, $(Ar_3Ge)_2O$. Similar treatment of the *o*-tolyl chloride gave the hydroxide, Ar_3GeOH.

Controlled dearylation by the action of gaseous hydrogen bromide upon tetraaryl compounds, in preliminary experiments with tetraphenyl- and tetra-*p*-tolylgermanium, effected replacement of one aryl group by bromine, yielding triarylgermanium bromide and aromatic hydrocarbon, both of which can be isolated. It is the purpose of work now in progress to attempt the use of this reaction in a study of the relative reactivities of various aryl groups when attached to germanium, analogous to the work of Kharasch, Bullard, Gilman and others,[8] on organic compounds of other elements.

Experimental

General

Germanium Tetrachloride.—Winkler[9] found that dry distillation of a mixture of mercuric chloride and germanium sulfide yields germanic chloride. Trials showed that recovery of germanium is high but the product somewhat impure. The results of distillations of mixtures of germanite and mercuric chloride showed that ordinary distillation from a flask transposed as high as 73% of the germanium to chloride; heating the mixture in a sealed tube at 260–290° transposed 97% of the germanium to chloride. This reaction might be used to prepare large quantities of the chloride and for analytical purposes is even more promising.

The germanium tetrachloride needed for the work described was prepared from 4.2 kg. of 100-mesh germanite (6.45% GeO_2) by decomposition with concentrated nitric acid, digestion of the dried insoluble residue with concentrated hydrochloric acid and distillation. The distillate of crude chloride was washed with concd. hydrochloric acid to remove arsenious chloride[10] and distilled through an all glass eight-ball Snyder column. The product (490 g., 87.5% recovery) boiled 83.0–83.8° corr. and gave no test for arsenic in the last fraction.

Bromotoluenes were obtained from Eastman Kodak Co. Anhydrous zinc chloride (Baker U. S. P.) was fused and then crushed and kept in a desiccator over phosphorus pentoxide. Eastman anhydrous ether was kept over sodium just before use. Tetraphenylgermane and triphenylgermanium bromide were prepared according to Kraus and Foster.[11] Grignard reagents were prepared in the usual way and in an atmosphere of nitrogen.

Analysis.—After a consideration of the available methods for the determination of germanium in organic compounds,[12] it seemed preferable to estimate carbon and hydrogen rather than germanium. Trials of a modification of the usual wet oxidation

(8) See, *e. g.*, Kharasch and Flenner, *J. Am. Chem. Soc.*, **54**, 674 (1932); Bullard and Holden, *ibid.*, **53**, 3150 (1931); Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932).

(9) Winkler, *J. prakt. Chem.*, [2], **36**, 188 (1887).

(10) Allison and Müller, *J. Am. Chem. Soc.*, **54**, 2833 (1932).

(11) Kraus and Foster, *ibid.*, **49**, 459, 460 (1927).

(12) Morgan and Drew, *J. Chem. Soc.*, **127**, 1767 (1925); Dennis and Hance, *J. Am. Chem. Soc.*, **47**, 374 (1925); Kraus and Brown, *ibid.*, **52**, 3693 (1930); Bauer and Burschkies, *Ber.*, **65**, 960 (1932); Tabern and Shelberg, *Ind. Eng. Chem., Anal. Ed.*, **4**, 402–403 (1932).

methods, using concd. and fuming sulfuric acid with solid ammonium persulfate followed by evaporation to GeO_2 in a silica beaker heated laterally by a ring-burner, gave results in three to five hours which were reproducible but low by about 0.6% due to mechanical loss during expulsion of fumes. Accordingly carbon and hydrogen were determined by the micro-method of Pregl.[13] Both a porcelain and a platinum boat were used, combustion occurring more readily in the latter. It was found advisable to cover the sample with a layer of previously ignited finely ground copper oxide. The compounds were with one or two exceptions difficult to burn, the last traces of carbon being extremely resistant to combustion, so that it was necessary to heat the tube until it just began to soften. Some of the substances with lower melting points ignited with a flash when too rapidly heated, but even with these all of the carbon could be burned only on strong ignition. The analyses reported below are in each case the average of three acceptable determinations.

Preparation of Tolyl Compounds of Germanium

Tetratolylgermanes—General Procedure.—Interaction of germanium tetrachloride, aryl bromide (*o*-bromotoluene), and sodium yielded unsatisfactory results. Interaction of the Grignard reagent and germanium tetrachloride yielded triarylgermanium bromide as the main product. The modified zinc aryl procedure described below, essentially that of Kraus and Foster,[14] was found satisfactory. The Grignard reagent dissolved in ether in a three-necked one liter flask equipped with a stirrer, reflux condenser and dropping funnel, reacted in an atmosphere of nitrogen with an ether suspension of zinc chloride. After refluxing for one-half to one hour the ether was replaced by toluene (or xylene). To the cooled mixture was added a solution of germanium tetrachloride in the same solvent. After standing overnight the mixture was heated on the water-bath for three hours and then stirred and refluxed for fifteen to twenty hours. Mechanical stirring was used throughout and was found to be noticeably more efficient than agitation by a stream of nitrogen. Ammonium chloride and dilute hydrochloric acid were used for the hydrolysis and yielded cleaner products than did 2 *N* sulfuric acid. The upper layer was dried by calcium chloride and distilled to a residue under reduced pressure. Further details are recorded in the descriptions of the individual compounds.

p-Tolyl Derivatives

Tetra-*p*-tolylgermanium.—*p*-Bromotoluene (100 g.), zinc chloride (33 g.) and germanium tetrachloride (13 g.) were treated as outlined above. The residue was dissolved in 50–60 cc. of benzene. To the warm solution was added an equal volume of 58–70° ligroin, the whole chilled strongly, and the separated solid washed with cold ligroin. The mother liquors yielded more crystals by the same procedure. The yield of pure product was 65%. It melted at 229° on the Dennis "melting point bar" and at 227° corr. in the usual apparatus.

Anal. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46. Found: C, 76.5; H, 6.47.

Tri-*p*-tolylgermanium Bromide.—Germanium tetrachloride (10.8 g.) was treated in ether solution with the Grignard reagent from 50 g. of *p*-bromotoluene. The mixture, after standing for two days, was refluxed for four hours. The ether was then distilled off and the residue heated at 110° for three hours.[15] The mass was taken up in benzene, decomposed with 2 *N* sulfuric acid, and the benzene layer dried with calcium chloride.

(13) Pregl, "Quantitative Organic Micro-analysis," tr. by Fyleman, P. Blakiston's Co. and Son, Philadelphia, 1924, pp. 15–72.

(14) Kraus and Foster, *J. Am. Chem. Soc.*, **49**, 459 (1927).

(15) Kraus and Flood showed this procedure to be advantageous in the preparation of tetraethylgermanium [*J. Am. Chem. Soc.*, **54**, 1636 (1932)].

The oily residue after distilling off the benzene was diluted with 20 cc. of 58–70° ligroin and the tetra-*p*-tolylgermanium filtered off; yield, 3.2 g.; 14.6%.

The mother liquors on vacuum distillation yielded (a) a small amount of *p*-bromotoluene, b. p. (760 mm.) 160–190°, (b) di-*p*-tolyl, b. p. (1–2 mm.) 100–125°, m. p. 117–121° from ligroin, and (c) a viscous oil of b. p. (1 mm.) 229–234° which after five recrystallizations from 90–120° ligroin was obtained as a crystalline solid of m. p. 130° corr. Mixed with a specimen of tri-*p*-tolylgermanium bromide (m. p. 127–128°) made according to Schwarz and Lewinsohn,[16] the melting point was 128–129°. This with the analytical and molecular weight values reported below identified the product as tri-*p*-tolylgermanium bromide. The yield after the first crystallization was 10.3 g. or 48%.

Anal. Calcd. for $C_{21}H_{21}GeBr$: C, 59.20; H, 4.97; mol. wt., 426. Found: C, 59.5; H, 5.24; mol. wt. (cryoscopic in benzene), 403, 404.

Tri-*p*-tolylgermanium Oxide.—Slightly impure tri-*p*-tolylgermanium bromide (1.9 g. from the Grignard reaction) was refluxed for ten hours with 40 cc. of 0.5 *N* aqueous sodium hydroxide. The resulting solid was filtered off and the filtrate titrated with 0.5 *N* hydrochloric acid. (Bromine found by titration, 18.3; calcd., 18.8.)

The white solid after drying and several crystallizations from 90–120° ligroin, and from a mixture of ligroin and methyl alcohol, melted at 147–148° corr.

Anal. Calcd. for $C_{42}H_{42}Ge_2O$: C, 71.23; H, 5.98; mol. wt., 708. Found: C, 70.6; H, 6.09; mol. wt. (Rast), 753; (cryoscopic in benzene), 714.

Tri-*p*-tolylgermanium oxide is a white densely crystalline solid, crystallizing in well-developed very small anisotropic prisms. It is insoluble in water; very slightly soluble in methyl and ethyl alcohol; and soluble in hot ligroin and cold benzene.

This compound was also made by the action of alcoholic silver nitrate on the bromide. The crystals obtained melted at 148–150° corr.

m-Tolyl Derivatives

Tetra-*m*-tolylgermanium.—The Grignard reagent from *m*-bromotoluene (75 g.), zinc chloride (30–33 g.), and germanium tetrachloride (10–11 g.) reacted as described above. The ether was removed by gentle heating (below 80°). After the usual further procedure there was obtained a final residue which was purified by crystallization from 58–70° ligroin; yield, 75%. Repeated crystallizations from 58–70° ligroin or a mixture of 90–120° ligroin and alcohol yielded the pure compound of melting point 146° corr.

Anal. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46; mol. wt., 437. Found: C, 76.5; H, 6.61; mol. wt. (cryoscopic in benzene), 405.

Tetra-*m*-tolylgermanium is a white solid crystallizing from ligroin in long thin needles, which exhibit parallel extinction. It reacts with bromine to form tri-*m*-tolylgermanium bromide. It is insoluble in water; very slightly soluble in hot or cold methyl alcohol; soluble in ligroin or carbon tetrachloride, and very soluble in benzene or toluene.

Tri-*m*-tolylgermanium Chloride.—The mother liquors from crystallization of several preparations of tetra-*m*-tolylgermanium were vacuum distilled. Di-*m*-tolyl was isolated boiling at 120–125° at 1–2 mm. and at 280–290° at atm. pressure. The only other isolable product was a viscous oil boiling at 221–224° (1–2 mm.). Crystallization from dry methyl alcohol gave fine silky needles melting at 79° to a cloudy liquid which cleared at 90°. Analysis identified this as tri-*m*-tolylgermanium chloride with a trace of a bromine-containing impurity.

(16) R. Schwarz and Lewinsohn, Ref. 1, p. 2354.

Anal. Calcd. for $C_{21}H_{21}GeCl$: C, 66.10; H, 5.55; mol. wt., 381. Found: C, 66.4; H, 5.51; mol. wt. (Rast), 445.

This compound was made also by warming tri-*m*-tolylgermanium oxide (see below) with concd. hydrochloric acid and alcohol on the water-bath. Evaporation of the alcohol and crystallization from methyl alcohol gave a product of m. p. 84–85° corr. A mixed melting point with the chloride obtained as by-product was 81.5–82.5° corr.

Tri-*m*-tolylgermanium chloride is a white solid crystallizing in fine optically active needles exhibiting parallel extinction. It is soluble in ligroin or benzene, and nearly insoluble in cold methyl alcohol.

Tri-*m*-tolylgermanium Bromide.—Tetra-*m*-tolylgermanium (25 g.) dissolved in 400 cc. of carbon tetrachloride was treated with 9.2 g. of bromine in 50 cc. of carbon tetrachloride added over a period of two hours. On refluxing the color gradually disappeared. After filtering with charcoal, the straw-yellow solution was distilled under slightly reduced pressure. *m*-Bromotoluene distilled at 128–129° at 135 mm.; b. p. 181–184° at 763 mm.; yield, 4.5 g. (46%).

The oily residue (25.0 g.) was crystallized from 400 cc. of hot methyl alcohol; yield, 15.8 g.; 65%. Two more crystallizations raised the melting point to 78.0–78.9° corr. The boiling point was 222–223° at 1 mm.

Anal. Calcd. for $C_{21}H_{21}GeBr$: C, 59.20; H, 4.97. Found: C, 59.1; H, 4.90.

Tri-*m*-tolylgermanium bromide is finely crystalline and white, but acquires a slight brown tinge on standing. It crystallizes in small, imperfectly formed, anisotropic needles. It is soluble in carbon tetrachloride, benzene and ether.

Tri-*m*-tolylgermanium Oxide.—The impure bromide (3.4 g.) from the mother liquors of the above preparation was shaken and then warmed with 150 cc. of a 1% alcoholic silver nitrate solution. The filtered solution was evaporated, the residue washed with water, taken up in benzene, dried with calcium chloride, and the solvent evaporated (yield, the theoretical). The product, crystallized three times from ligroin, melted at 125.0–125.2° corr.

Anal. Calcd. for $C_{42}H_{42}Ge_2O$: C, 71.23; H, 5.98; mol. wt., 708. Found: C, 71.0; H, 5.93; mol. wt. (cryoscopic in benzene), 686.

Tri-*m*-tolylgermanium oxide crystallizes in thick ill-formed crystals. It reacts with concd. hydrochloric acid in alcoholic solution to form tri-*m*-tolylgermanium chloride as described above. It is soluble in alcohol and benzene, and is insoluble in water.

Triphenyl-*m*-tolylgermanium.—Triphenylgermanium bromide (5 g.) and *m*-tolylmagnesium bromide reacted in the usual manner[17] and gave a product melting at 132–133° corr. Its analysis is reported below. A further crystallization from methyl alcohol raised its melting point to 136–138° corr. Attempts to repeat this experiment using twice the quantity of bromide were unsuccessful due to the large amount of triphenylgermanium oxide which was formed from unreacted bromide. The following procedure was better.

The zinc aryl compound from 20 g. of *m*-bromotoluene reacted in benzene solution with 6.0 g. of triphenylgermanium bromide. The mixture was refluxed for fourteen hours and then decomposed with ammonium chloride. The residue from distillation of the benzene layer deposited crystals which were washed with alcohol and dried; yield, 5.3 g.; 86%; m. p. 144–147° corr. After two crystallizations from alcohol and ligroin the substance was extracted eleven times with small quantities of methyl alcohol. This served to separate a high melting insoluble impurity and yielded a specimen of triphenyl *m*-tolylgermanium, resembling the above product under the microscope, and melting at 136.5–138.5° corr. A mixed melting point test gave the value 136–138° corr.

(17) Orndorff, Tabern and Dennis, *J. Am. Chem. Soc.*, **49**, 2513 (1927).

Anal. Calcd. for $C_{25}H_{22}Ge$: C, 75.99; H, 5.62; mol. wt., 395. Found: C, 75.9; H, 5.97; mol. wt. (cryoscopic in benzene), 379.

Triphenyl *m*-tolylgermanium crystallizes from hot methyl alcohol in small strongly anisotropic needles which exhibit parallel extinction. It is soluble in benzene and hot ligroin; insoluble in cold ligroin, methyl and ethyl alcohols. Small amounts are best crystallized from methyl alcohol; larger amounts from a mixture of alcohol and ligroin.

o-Tolyl Derivatives

Tetra-*o*-tolylgermanium.—This compound was prepared according to the general procedure. The quantities were the same as for the *m*-tolyl compound; xylene was used as solvent in place of toluene. The oily residue was diluted with 20 cc. of 58–70° ligroin, and on standing yielded a solid product which was filtered off and washed with 58–70° ligroin. The melting point was 162–165° corr.; yield, 7.8 g.; 30%. The product was crystallized by boiling with 150 cc. of alcohol and enough benzene to clear the solution, which was filtered hot and chilled, yielding 4.9 g. of white, dense crystals of m. p. 173–174.5° corr. A specimen purified by repeated crystallization from 90–120° ligroin and then from a mixture of alcohol and benzene had a sharp melting point of 175–176° corr.

Anal. Calcd. for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46; mol. wt., 437. Found: C, 76.9; H, 6.48; mol. wt. (cryoscopic in benzene), 392.

When crystallized from alcohol and benzene, crystals of the tetra-*o*-tolyl compound appear slowly and are usually badly developed, although their hexagonal character is easily observed under the microscope. The compound is insoluble in water, cold alcohol and light ligroin; slightly soluble in hot alcohol; and soluble in carbon tetrachloride, benzene, xylene or hot ligroin.

Tri-*o*-tolylgermanium Bromide.—A solution of tetra-*o*-tolylgermanium (4.0 g.) when refluxed with an equivalent quantity of bromine in 50 cc. of pure carbon tetrachloride was rapidly decolorized with the evolution of hydrogen bromide. Distillation of the solution yielded at 205–210° (1 mm.) a colorless oil with a bluish fluorescence. The product contained bromine. The molecular weight in benzene was 409; calcd. for $C_{21}H_{21}GeBr$, 426.

Tri-*o*-tolylgermanium Chloride.—The ligroin extract from the preparation of tetra-*o*-tolylgermanium was distilled *in vacuo*. After removal of some di-*o*-tolyl (b. p. (760 mm.) 272–282°), three fractionations at 1–2 mm. yielded finally a yellowish resinous oil with a bluish fluorescence which boiled at 229–235° at less than 1 mm. Its analysis indicated it to be probably a mixture of tri-*o*-tolylgermanium chloride and tetra-*o*-tolylgermanium.

Anal. Calcd. for $C_{21}H_{21}GeCl$: C, 66.10; H, 5.55; for $C_{28}H_{28}Ge$: C, 76.92; H, 6.46. Found: C, 74.0; H, 6.19.

Slow evaporation of an alcohol solution of this product deposited a solid which after crystallization from alcohol melted at 157–161°; it had the characteristic crystal form of tetra-*o*-tolylgermane under the microscope. The mother liquor from the first separation of the product was freed from alcohol and the residue distilled. It boiled at 216–222° at 1 mm. and treated with alcoholic silver nitrate yielded tri-*o*-tolylgermanium hydroxide, indicating it to be probably tri-*o*-tolylgermanium chloride.

Tri-*o*-tolylgermanium Hydroxide.—Tri-*o*-tolylgermanium chloride (4.0 g.) obtained as just described (b. p. (1 mm.) 215–219°) was treated with an excess of alcoholic silver nitrate. The filtrate, worked up as outlined under tri-*m*-tolylgermanium oxide, yielded an oily residue which would not crystallize but which distilled at 212–214° (1 mm.) as a resinous oil. On standing it became crystalline. From hot methyl alcohol it deposited as an amorphous powder. Qualitative tests showed the absence of halogen.

Anal. Calcd. for $C_{21}H_{22}GeO$: C, 69.46; H, 6.11; mol. wt., 363. Found: C, 69.6; H, 6.12; mol. wt. (cryoscopic in benzene), 344.

The Controlled Action of Hydrogen Bromide on Tetraarylgermanium Compounds

Tetraphenylgermanium.—An excess of hydrogen bromide was passed at room temperature through a solution of tetraphenylgermane (3.0 g.) in 100 cc. of chloroform. The solution was distilled to a residue which was crystallized twice from 90–120° ligroin. The crystals of triphenylgermanium bromide melted at 138.2° corr.

Tetra-*p*-tolylgermanium.—A 30% excess of hydrogen bromide reacted at room temperature with the germane (3.0 g.) in 100 cc. of chloroform. The solution was fractionally distilled and 3.2 cc. collected between 66 and 110°. Refractionation of this product yielded toluene, identified as 2,4-dinitrotoluene, m. p. 70–71° corr.[18]

The residue of 3.1 g. (2.9 g. calcd.) was crystallized from 58–70° ligroin. It melted at 124–128.5° obs.; mixed with tri-*p*-tolylgermanium bromide (m. p. 128–129.5° obs.) the melting point was 127–129.5° obs.

Summary

1. The following new tolyl compounds of germanium have been prepared and characterized: tetra-*o*-tolylgermanium, tetra-*m*-tolylgermanium, tri-*o*-tolylgermanium bromide, tri-*m*-tolylgermanium bromide and chloride, tri-*o*-tolylgermanium hydroxide, tri-*m*-tolylgermanium oxide, tri-*p*-tolylgermanium oxide, triphenyl-*m*-tolylgermanium.

2. The zinc aryl procedure of Kraus and Foster has been used successfully in the preparation of tetratolylgermanes, including tetra-*p*-tolylgermanium, and the mixed compound triphenyl-*m*-tolylgermanium.

3. Interaction of germanium tetrachloride and *p*-tolylmagnesium bromide yielded principally tri-*p*-tolylgermanium bromide, indicating the probable cause of low yields of tetraarylgermanes hitherto obtained by this method.

4. Controlled action of hydrogen bromide on tetraphenyl- and tetra-*p*-tolylgermanium yielded the corresponding triarylgermanium bromide and aromatic hydrocarbon.

(18) Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, Vol. I, 1904, p. 202.